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The concept and theory of method detection limit are developed in detail. Applications of the method detection limit to the analysis of organics by the EPA 600 series methods are presented with an interpretation of the results.

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Journal Article

Trace analyses for wastewaters

Method detection limit, a new performance criterion for chemical analysis, is defined as that concentration of the analyte that can be detected at a specific confidence level. Both theory and applications are discussed for reliable wastewater analyses of priority pollutants

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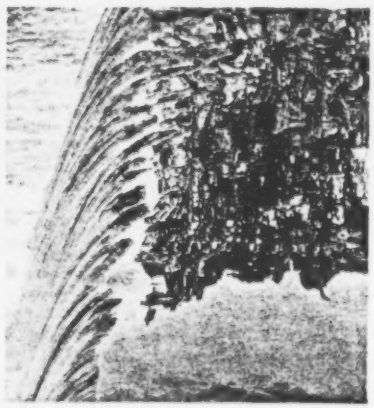
The development of trace analysis methodology brought with it a series of questions about method performance at low concentration levels of analyte (*1*, *2*, *3*). Under Section 304(h) of the Clean Water Act, as amended in 1977, (*4*) the Environmental Monitoring and Support Laboratory (EMSL) in Cincinnati is responsible for providing test procedures for the measurement of specified pollutants at trace concentrations in municipal and industrial wastewaters.

A series of procedures was published in the Federal Register for the analysis of the 129 priority pollutants (*5*). These procedures are designed to monitor direct discharges from industrial and publicly owned treatment works (POTW), sources under the National Pollutant Discharge Elimination System (NPDES), and discharges into a POTW system under pretreatment regulations. The 304(h) monitoring methods for organic analyses are of two types:

- 12 methods designed around gas–liquid and high performance liquid chromatography with standard detectors and modest operational skill requirements for the permit holder
- three methods that employ a mass spectrometer as a detector for multiple measurements with minimal interference.

To meet the needs associated with these methods for analysis of the priority pollutants, it was incumbent on EMSL to develop method performance characteristics for these methods. As advocated by Wilson (*6*), method performance characteristics are specified criteria that detail the ability of a method to analyze for analyte.



Clearly, analyte detection is a fundamental criterion of performance for an analytical system. Any analytical system is constrained by an inability to discern the signal due to noise from the signal due to the presence of analyte at low concentrations. The limit of detection for a given analyte can be defined as that concentration of the analyte which can be detected at a specific confidence level.

The concept of detection limit has been the focus of debate (*7*). The controversy generally centers on definitions that vary with the analyst (*8*). Confusion arises when instrumental and method detection limits are compared and sometimes used interchangeably (*9*). Moreover, detection and determination have also been conceptually intertwined by some investigators (*10*). Although definitions of the detection limit for a given analyte vary, investigators concur that the detection limit should be related to the standard deviation of the measured values at or near zero concentration of the analyte (*11*).

There is no doubt that the detection limit is one of the most important performance characteristics of an analytical procedure. In most cases, a detection limit must be viewed as a temporary limit to current methodology.

Complete analytical system

Ostensibly, analysts do not directly observe concentrations of analyte. The measurements of the transducer signal, which are related to the analyte concentration, are actually observed. In any analytical system, information concerning the identity and quantity of an analyte is contained in the analytical signal, which depends on a large number of experimental variables. Since these variables contain a random component, the analytical signal will also have a random component characterized by a probable uncertainty. Some part of an averaged signal must be a function of the true analyte concentration. Analysis of the signal precludes the ability of the analyst to discern the fluctuations of the background from the average value of the analytical signal for a given concentration of analyte.

The relationship between background noise and analytical signal has been studied by many authors; their work has helped to develop the definition and evaluation of the detection limit. A point of reference is necessary to specify the sources of background noise contributing to the overall analytical signal. Kaiser (*12*) has been a major figure in this development. He has centered his thoughts on the detection limit of a "complete analytical procedure." Such a procedure or method is specified in every detail by

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fixed working directions (order of analysis) and is directed for use at a particular analytical task. The specifics of a "complete analytical procedure" include a predetermination of everything associated with the analytical task: the apparatus, the external conditions, the experimental procedure, the evaluation of results, and calibration of the analytical system. Thompson and Howarth (*13*) have expanded this concept to develop an analytical system that comprises:

- a set of samples of the analyte in a specific matrix
- an exactly defined analytical procedure
- the particular instrumentation used.

The purpose for developing a procedure to evaluate detection limits was to design a methodology not limited by instrumentation or analytical methodology. For pragmatic reasons, we focused on an operational definition of detection limit. The analytical methodology for priority pollutants served as a basis for the concepts concerning the method detection limit (MDL). Each of the methods comprising this methodology is designed to constitute a "complete analytical procedure" or "complete analytical system." Integral to these concerns was an attempt to specify a parameter for performance measurement of each method of analysis.

The method detection limit refers to samples processed through all the steps comprising an established analytical procedure. The fundamental difference between our approach to detection limit and former efforts is the emphasis on the operational characteristics of the definition. MDL is considered operationally meaningful only when the method is truly in the detection mode, i.e., analyte must be present. *The method detection limit is defined as the minimum concentration of a substance that can be identified,*

Theory

The MDL can be presented as an error distribution. The definition of MDL implies that, on an average, 99% of the trials measuring the analyte concentration at the MDL must be significantly different from zero analyte concentration. A one-sided test is performed to evaluate this hypothesis.

This graphical description of MDL is based on the assumptions that the error distribution associated with the analytical measurement, in a sufficiently large neighborhood proximate to the MDL, has a relatively homogeneous variance and is normally distributed. A sufficiently large neighborhood is specified to accommodate our recommendations for the initial estimate of the MDL.

Basic to these concepts is the assumption that the variability of an analytical measurement, as measured by the standard deviation σ_C, is a function of the concentration being measured $\sigma_C = f(C)$. Experience has shown that the variance is relatively homogeneous over a relatively large concentration range. Alternatively, one may say that the variability is reasonably smooth over the linear range of an analytical method. Such a functional response can be approximated by a polynomial of degree N.

$$\sigma_C = k_0 + k_1C + k_2C^2 \ldots + k_NC^N \quad (1)$$

Since economic considerations demand that the MDL be determined with a limited number of analyses, the standard deviation S_c employed in these calculations is an estimate of the population standard deviation σ_c. If the mass of the standard addition (spike) is measured accurately, the coefficients and intercept for the polynomial model may be estimated by linear regression. This model can be truncated to a first order equation:

$$S_c = k_0 + k_1C \quad (2)$$

The form of the error distribution associated with these considerations is irrelevant, but we assumed that the number of independent error components, associated with most analytical systems, will be large enough to invoke the central limit theorem. Therefore, the normal distribution will be a good approximation of the error distribution associated with any analytical determination (*16, 17*).

To help avoid a negative estimate of k_0, the regression equation can be transformed by dividing through by C.

$$\frac{S_c}{C} = \frac{k_0}{C} + k_1 \quad (3)$$

A regression on S_c/C vs. 1/C will yield the estimated slope k_0 and the intercept k_1. The estimate of the slope should be less sensitive to nonrandom errors than the intercept estimate. Hence, a negative estimate of k_0 often may be avoided.

Since a limited number of samples will be taken at each concentration, the error distribution of this sampling is expected to be approximated by a student's t distribution. By defining t_c as:

$$t_c = \frac{C}{S_c/(N)^{1/2}} \quad (4)$$

then

$$\frac{(N)^{1/2}}{t_c} = \frac{S_c}{C} \quad (5)$$

and the regression equation becomes:

$$\frac{(N)^{1/2}}{t_c} = \frac{k_0}{C} + k_1 \quad (6)$$

The regression equation is now in a form compatible to find MDL, such that

$$t_c \approx t_{(N-1\ df,\ 1-\alpha=.99)}$$

or

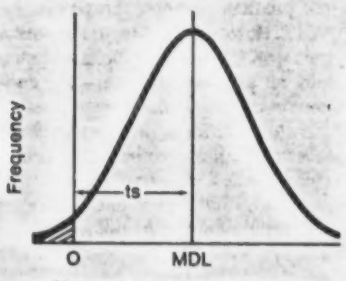
$$\text{MDL} = \frac{t_{(N-1\ df,\ 1-\alpha=.99)}\ k_0}{(N)^{1/2} - k_1 t_{(N-1\ df,\ 1-\alpha=.99)}} \quad (7)$$

It must be emphasized that k_0 is conceptually no longer the sample standard deviation at zero concentration, a concept which necessitates the possibility of negative analytical responses at zero concentration of analyte. Now k_0 is the linear trend in the regression of $(N)^{1/2}/t_c$ vs. 1/C, which in practical terms means that analytical responses at zero concentration are not necessary or implied in the determination of MDL. For obvious economic reasons, the equation for MDL can be reduced to:

$$\text{MDL} = t_{(N-1\ df,\ 1-\alpha=.99)}S_c \quad (8)$$

by setting the intercept k_1 to be equal to zero and setting $k_0/(N)^{1/2}$ equal to S_c, where S_c refers to the standard deviation of replicate determinations at a fixed concentration.

The theory: method detection limit depicted as an error distribution



measured, and reported with 99% confidence that the analyte concentration is greater than zero and is determined from replicate analyses of a sample of a given matrix containing analyte (14).

Single step procedure

The procedure for determining MDL is based on the analysis of seven samples of the matrix containing analyte. If the MDL is to be determined in reagent (blank) water, a laboratory standard of the analyte in reagent water is prepared at a concentration at least equal to or in the same concentration range as the estimated MDL. We recommend that the analyte be added to the water to give a final concentration between one and five times the estimated MDL. When the MDL is to be determined in a sample matrix other than reagent water, analysis of the sample background is required.

If the measured level of analyte is less than the estimated MDL, the analyte is spiked into the matrix to bring the level of analyte to a concentration between one and five times the estimated MDL. Should the measured level of analyte be greater than five times the estimated MDL, two options exist:

- the analyst is required to obtain another sample of the same matrix with a lower level of analyte present
- the sample may be used as is for the MDL determination if the analyte level does not exceed 10 times the MDL of the analyte in reagent water.

The error variance of the analytical method changes as the analyte concentration increases above MDL. Hence, MDL values determined in a matrix containing a high analyte concentration may not truly reflect method error variance at lower analyte concentrations.

A minimum of seven aliquots of matrix are processed through the entire analytical method and the MDL is calculated. All concentration calculations are made according to the defined method, with final results expressed in the method reporting units. If a blank measurement is required to calculate the measured level of analyte, the analyst must obtain a separate blank measurement for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.

It may be economically and technically desirable to evaluate the estimated MDL before proceeding with the analysis of the seven aliquots. This will prevent repeating the entire procedure and ensure that the MDL determination is being conducted at the correct concentration. It is quite possible that an incorrect MDL could be calculated from data obtained at many times the actual MDL even though the level of analyte would be less than five times the calculated method detection limit.

To ensure that the estimate of the method detection limit is a good estimate, the analyst must determine that a lower concentration of analyte will not result in a significantly lower calculated MDL. We recommend initial analysis of two aliquots of the sample for this purpose. Should these measurements indicate that the sample is in the desirable range for the MDL determination, five additional aliquots are processed through the MDL procedure. If the sample is not in the correct range, the MDL must be reestimated and seven new aliquots of the sample matrix processed as described.

The standard deviation of the seven replicate measurements is calculated and the MDL is computed as

$$MDL = t_{(N-1,1-\alpha=.99)} \times S_c \quad (9)$$

where:

$t_{(N-1,1-\alpha=.99)}$

Testing the theory

This theory is tested by collecting data from a limited number of samples at a single concentration estimated to be in a sufficiently large neighborhood proximate to the MDL. The directions given to guide the analyst in estimating the MDL are the following:

- the concentration value that corresponds to an instrument signal/noise in the range of 2.5–5. If the criteria for qualitative identification of the analyte is based upon pattern recognition techniques, the least abundant signal necessary to achieve identification must be considered
- the concentration value that corresponds to three times the standard deviation of replicate instrumental measurements for the analyte in reagent water
- the concentration value that corresponds to the region of the standard curve where there is a significant change in sensitivity at low analyte concentrations, i.e., a break in the slope of the standard curve
- the concentration value that corresponds to known instrumental limitations.

The analyst's experience is not intended to supersede any of the other considerations, but it does provide for crucial input of any relevant background with which a decision can be reached if the other directions for estimation are either inoperative or do not give a clear choice for estimating the MDL.

Invoking these criteria for estimation of the MDL involves a risk such that if the initial estimates of the MDL are not proximate to the (true) MDL, the calculated MDL will be much in error. The assumptions involved in the estimation of the MDL can be tested in one of two ways:

1. The estimated MDL is equal to the calculated MDL, if the 95% confidence interval of the calculated MDL contains the estimated MDL value.
2. If the condition set forth in item 1 is not satisfied, then an iterative procedure, where the most recent calculated MDL value is used as the next estimated MDL, must be used until the variances of successive iterations do not differ using the F test.

Clearly, the MDL is prescribed by any attending instrumental detection limits. The procedure to determine the MDL was designed to apply to a wide variety of sample matrices ranging from reagent (blank) water containing analyte to wastewater containing analyte. Thus, the MDL for an analytical procedure may vary as a function of the sample type (matrix). The developed procedure requires a complete, specific, and well-defined analytical method. All sample processing steps of the analytical method must be included in the determination of the method detection limit.

A crucial point is that the MDL for a given analyte in a given matrix does not preclude quantitation below the MDL. However, when quantitation below MDL is pursued, the confidence interval estimate of an analyte concentration below MDL will be greater than at MDL for a given confidence level and a given analytical effort. In other words, it would require a greater number of samples to analyze for an analyte concentration below MDL to achieve the same confidence limits attached to the MDL.

is the student's t value for a one-tailed test at the 99% confidence level with $N - 1$ degrees of freedom. S_c is the standard deviation of the seven replicate analyses. Confidence-interval estimates for the MDL are computed using percentiles of the chi square over degrees of freedom distribution (χ^2/df). The 95% confidence limits for the MDL are computed in Equations 10 and 11:

$$\frac{UCL_{MDL}}{P_{.025}} > MDL > \frac{LCL_{MDL}}{P_{.975}} \quad (10)$$

where the percentile values are obtained from the χ^2/df distribution for the associated degrees of freedom ($df = 6$).

$$LCL_{MDL} = 0.64\ MDL$$
$$UCL_{MDL} = 2.20\ MDL \quad (11)$$

The confidence limit expressions reduce to Equation 11 where LCL_{MDL} and UCL_{MDL} are the lower and upper 95% confidence limits of the MDL based upon the analysis of seven aliquots.

Iterative procedure

An additional procedure is presented to test the reasonableness of the MDL estimate and subsequent MDL determinations on the same matrix. The initial calculated MDL is tested by spiking the matrix at the calculated MDL and processing the seven samples through the entire MDL procedure. At each iteration of the MDL calculation, the variance from the current MDL calculation and the variance of the preceeding MDL calculation are compared by computing the F-ratio, which is compared with the tabulated F-ratio, $F_{0.95(6,6)} = 3.05$. If the computed F-ratio is less than 3.05, then the pooled standard deviation is calculated using the standard deviation of the current MDL determination and the preceeding iteration. The MDL is then calculated in Equation 12:

$$MDL = 2.681 \times S_{pooled} \quad (12)$$

where:

2.681 is equal to $t_{(12,\ 1-\alpha=.99)}$

and $S_{pooled} = [(S_A^2 + S_B^2)/2]^{1/2}$

The confidence levels for the MDL of the iterative procedure are computed from the percentiles of the chi squared over degrees of freedom distribution with degrees of freedom ($N = 12$) based on 14 aliquots. Two degrees of freedom are lost in the calculation of the averages of the two sets of seven aliquots.

The confidence limit expression for the MDL based on the iterative procedure reduces to

$$LCL_{MDL} = 0.72\ MDL$$
$$UCL_{MDL} = 1.65\ MDL \quad (13)$$

where LCL_{MDL} and UCL_{MDL} (13) are the lower and upper 95% confidence limits of the MDL based on the analysis of 14 aliquots.

When the analyte is present in the matrix at a relatively "high" concentration, measurement of the MDL is not meaningful. If the analyte is found at a relatively "low" level in the sample matrix, the sample at that analyte concentration may be used as the initial estimate of the MDL, and the sample aliquots processed through the MDL procedure. However, if the calculated MDL is lower than the background level of analyte present in that matrix, the iterative procedure cannot be used. Convergence of the iterative procedure will depend on the closeness of the estimated MDL, or the background level of analyte present in the matrix, to the calculated MDL.

Reporting information

The analytical method used must be specifically identified by number or title and the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options affecting the method detection limit, such options must be specified with the MDL value. The analyst must also report the mean analyte level and specify the matrix used with the MDL. If a laboratory standard or a sample that contained a known amount of analyte was used for this determination, the mean recovery must also be reported. If the level of analyte in the sample is below the determined MDL or does not exceed 10 times the MDL of the analyte in reagent water, no MDL value is reported.

Applications

Method detection data were collected for the organic priority pollutant methods and are displayed in Tables 1–5. Data for Method 603-acrolein and acrylonitrile are currently unavailable. The earlier estimates of detection limits cited in Reference 5 were based solely on signal-to-noise criteria.

Some of the reported MDL values in the tables are at concentrations higher than had been anticipated. Low values for MDL are closely tied to the learning curve of each method. Experience has demonstrated that the analyst who has extensive experience with a given method is more likely to generate lower MDL values than an analyst with only cursory experience with the method.

The optional iterative scheme was developed as a response to high MDL values in these tables. These larger values are attributed to a mistaken estimate of the MDL. The closeness of the initial estimate to the final calculated MDL is a critical concern in using this procedure. The tables are organized according to each method and its particular set of analytes. Background, spike level, percent recovery, and matrix types are included as specified in the reporting requirements for the MDL.

Some analytes in Tables 2 and 3 gave wastewater background levels that range from 18 to 90 000 times larger than the respective reagent water MDL value; therefore, no wastewater MDL value should be reported. However, the wastewater MDL values are included to illustrate that the MDL procedure can give meaningless values when the analyte or analyte plus interference is present at levels much larger than 10 times the MDL value in reagent water.

For these analytes, the calculated wastewater MDL values averaged 240 times larger (range 6 to 1150) than the respective reagent water MDL value. There are analytes in Table 2 that exhibited wastewater background levels that range from 0.8 to 8 times the respective MDL value in reagent water. The MDL procedure gave meaningful values for these analytes since the wastewater MDL values averaged 2 times larger (range 0.4 to 9) than the respective reagent water MDL values.

Method 602—purgeable aromatics

This is not a purge-and-trap method using packed column gas chromatography and a photoionization detector. The MDL values listed in Table 1 for the purgeable aromatics are quite reasonable for reagent water although, except for toluene, the recoveries are consistently over 100%. The MDL values calculated for the two wastewaters are derived from background analyte levels when the analyte was present in the wastewater and from spike levels when absent. Recoveries and MDL values for analytes spiked into wastewater No. 1 are reasonable but the MDL value based on the background concentration of 1,2-dichlorobenzene is not. The MDL value for 1,2-dichlorobenzene reflects a large variation in the analyte background level. However, the MDL value loses its meaning since the analyte is present

TABLE 1

Method detection limit for purgeable aromatics as analyzed by Method 602 (*22*)

Compound	Reagent water			Wastewater No. 1[a]				Wastewater No. 2[b]			
	Spike level (μg/L)	Average % recovery	MDL (μg/L)	Background	Spike level (μg/L)	Average % recovery	MDL (μg/L)	Background	Spike level (μg/L)	Average % recovery	MDL (μg/L)
Benzene	0.5	131	0.2	0.4	0.0	—	1.74	41	0.0	—	30.0[c]
Toluene	0.5	80	0.2	3.6[c]	0.0	—	1.55[c]	538	0.0	—	230[c]
Ethyl Benzene	0.5	120	0.2	0.0	0.5	100	0.2	70	0.0	—	34[c]
Chlorobenzene	0.5	120	0.2	0.0	0.5	60	0.2	469	0.0	—	197[c]
1,2-Dichlorobenzene	0.5	120	0.4	34[c]	0.0	—	20[c]	1.8	0.0	—	0.4[c]
1,3-Dichlorobenzene	0.5	120	0.4	0.0	0.5	80	0.3	1.6	0.0	—	1.0
1,4-Dichlorobenzene	0.5	140	0.3	0.0	0.5	140	0.4	7	0.0	—	1.7[c]

[a] Effluent from chemical intermediates manufacturer.
[b] Effluent from rubber, plasticizers and specialty chemicals manufacturing facility.
[c] Background greater than 10 times calculated MDL in reagent water.

in determinable quantities. The MDL values in wastewater No. 2 are similarly inflated.

Method 605—benzidines

This is a HPLC method using reverse-phase chromatography and an electrochemical detector. The MDL value for benzidine in reagent water was determined using an electrochemical detector potential of +0.8 V vs. S.C.E., while in the two wastewaters, the MDL was determined using a potential of 0.6 V due to the presence of interfering peaks at 0.8 V. Reducing the potential gives more specificity for benzidine but also lowers the instrumental sensitivity. Dichlorobenzidine was determined at +0.8 V in all matrices. The estimated MDLs published with the earlier version of this method (*5*) have nearly been achieved. In the reagent water and wastewater No. 1, the MDLs are within a factor of two of those originally estimated, while for wastewater No. 2 they are approximately a factor of 4 higher for benzidine and a factor of 2 higher for dichlorobenzidine. Recoveries of 60–70% for benzidine and 50–70% for dichlorobenzidine were achieved, similar to those obtained in the original method development. To achieve these MDLs, it was important to eliminate all oxidizing agents from the sample matrix. Residual chlorine, which is recognized as a notorious oxidant, was decomposed by adding 35 mg/L sodium thiosulfate to each wastewater and reagent water. The reagent water was adjusted to a neutral pH prior to spiking the sample matrix with analyte.

The low recoveries at low spiking levels are probably due to oxidation during sample processing. Since such oxidation reactions are overall second order processes (first order in both oxidant and amine), low recovery of the amine can occur at low concentrations of analyte and relatively large concentration of oxidants.

Organochlorine pesticides and PCBs

Method 608 is a GC method using packed column chromatography and an electron capture detector (ECD). The MDL values of the pesticide and PCB analytes in reagent water listed are generally equal to or lower than those reported as estimates with the earlier version of this method (*5*). Heptachlor epoxide analysis exhibited anomalous behavior in reagent water. This resulted from the presence of an interfering chromatographic peak that clearly coeluted with the compound, thus requiring blank measurements. In many instances, the level of this interference did not remain constant but was variable for the aliquots of a given matrix. In this case, the blank did not necessarily represent the background concentration of the interfering species in the sample. By averaging the background, we assume that a more reliable measure of the background is obtained.

The basic approach to determining MDLs in wastewater was the same as for reagent water. However, in the presence of coeluting or interfering substances, the analyst chose to modify the MDL procedure. In some cases, when the water contained pesticide or PCB analytes, direct calculation of the standard deviation was prevented by coeluting, interfering materials. Large fluctuations in the background were observed, which attenuated the utility of the blank measurements.

Since the response of an interfering species and analyte was being measured, the variability of the response represented the total variability due to both compounds. In this case the corrected variance of the sample, calculated by subtracting the variance of the background from the variance due to the analyte plus background was used to calculate the MDL. Two analytes in wastewater No. 1, endosulfan sulfate and γ-BHC, required this treatment. In wastewater No. 2, this alternate scheme of variance calculation was used for β-BHC, δ-BHC, γ-BHC, endosulfan sulfate, aldrin, and endosulfan II. The MDLs in wastewater No. 1 are fairly consistent but considerably higher than the reagent water MDL values. The MDL values for wastewater No. 2 compare more favorably to the reagent water than do those from wastewater No. 1,

TABLE 2

Method detection limit for benzidines as analyzed by Method 605 (*24*)

Compound	Reagent water			Wastewater No. 1[a]		Wastewater No. 2[b]	
	Spike level (μg/L)	Average % recovery	MDL	Average % recovery	MDL	Average % recovery	MDL
Benzidine	0.50	62	0.08	74	0.06[c]	74	0.19
Dichlorobenzidine	0.50	50	0.13	72	0.09	59	0.22

[a] Pigment manufacturing wastewater.
[b] Aniline manufacturing wastewater.
[c] Background was 0.06 μg/L.

TABLE 3

Method detection limits for pesticides and polychlorinated biphenyls as analyzed by method 608 (*25*)

Compound	Reagent water			Wastewater No. 1[a]			Wastewater No. 2[b]		
	Spike level (ng/L)	Average % recovery	MDL (μg/L)	Background level (ng/L)	Spike level (ng/L)	Average % recovery	MDL (μg/L)	Spike level (ng/L)	Average % recovery	MDL (μg/L)
α-BHC	9.6	99	.003	260[c]	0.0	—	0.184[c]	14.0	72	0.013
β-BHC	24.0	97	.006	—	30.0	164	0.059	30.0	94	0.011
δ-BHC	19.6	91	.009	—	43.0	84	0.062	43.0	94	0.023
γ-BHC	17.2	103	.004	—	20.0	320	0.283	20.0	101	0.007
DDD	52.0	100	.011	—	52.0	77	0.031	52.0	79	0.029
DDE	24.0	96	.004	—	20.0	129	0.038	20.0	71	0.008
DDT	70.0	99	.012	—	60.0	76	0.049	59.0	71	0.030
Endosulfan I	25.2	72	.014	—	45.0	76	0.061	73.0	99	0.056
Endosulfan II	48.0	97	.004	—	12.0	37	0.009	21.0	60	0.013
Endosulfan sulfate	272.0	81	.066	—	150.0	105	0.30	329.0	94	0.262
Heptachlor	11.6	91	.003	—	6.0	715	0.055	18.0	89	0.009
Heptachlor epoxide	18.4	153	.083	—	65.0	155	0.148	65.0	80	0.021
Aldrin	14.4	84	.004	—	20.0	140	0.055	20.0	80	0.0054
Dieldrin	30.4	100	.002	—	6.0	275	0.017	13.0	107	0.010
Endrin	43.2	101	.006	31[c]	0.0	—	0.079[c]	32.0	70	0.031
Chlordane	152.0	99	.014							
Toxaphene	156.0	99	.235							
PCB 1242	188.0	90	.065							

[a] Effluent from a pesticide manufacturing plant.
[b] Effluent from an organics and plastics manufacturing plant.
[c] Background greater than 10 times MDL in reagent water.

and reflect the lower background of electron capture-sensitive materials present in wastewater No. 2.

Polycyclic aromatic hydrocarbons

Method 610 is a reverse-phase HPLC method using UV and fluorescence detectors. From the data in Table 4, it is obvious that both recovery and precision for most of the PAHs were good, generally ±10% precision and 90–100% recovery, in all matrices. Fluoranthene was the only analyte that was significantly different. In one aliquot of reagent water, the result for fluoranthene was nearly twice the spike level. There is a possibility that this aliquot was doubly spiked; this would explain the unexpected accretion of analyte. Hence, the MDL for fluoranthene in reagent water is skewed toward a higher concentration because of the higher value of the standard deviation. Precision and recovery data for fluoranthene in the two wastewaters, one of which had a detectable background level of fluoranthene, were considerably better than in reagent water.

The fluoranthene MDL data for the wastewaters is probably a better indication of the precision of the method, providing that blank contamination is not a problem. The single reagent water aliquot giving a high result for fluoranthene was probably contaminated in some way. On occasion, fluoranthene has been observed at low concentration levels in reagent water; this points to fluoranthene as being the PAH analyte most likely to present contamination problems. This observation is more credible since fluoranthene is a highly fluorescent compound under Method 610 assay conditions, and is one of the most commonly found PAHs in environmental samples.

The MDL values obtained for the PAH analytes in these three water matrices are all equal to or lower than those estimated in the earlier version of the method (except for fluoranthene in reagent water).

2,3,7,8-Tetrachlorodibenzo-*p*-dioxin[30]

Method 613 is a gas chromatography/mass spectrometry (GC/MS) method that requires use of a capillary column, which uniquely separates 2,3,7,8-TCDD from the other 21 TCDD isomers and specifies operating the MS detector in the selected ion monitoring mode (SIM) of data acquisition. The MDL value for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) in reagent water is 0.002 μg/L and is slightly lower than the detection limit given in the earlier version of this method (*5*). The spiking level in reagent water was 5.0 ng/L, which gave an average recovery of 95%.

This method has extremely high selectivity and sensitivity for 2,3,7,8-TCDD. Qualitative identification is based on pattern recognition using the ratio of the response for the ions at m/z 320, 322, and 257. The seven aliquots of reagent water at 5 ng/L gave an average ratio of 0.79 ± 0.04 for the ions at m/z 320 and 322.

The response for the ion at m/z 257 is approximately 30% of the response for the ion at m/z 322. Refinement of the MDL value through reiteration of the MDL procedure using a spiking level of 2 ng/L will demonstrate that the MDL is not significantly lower than 2 ng/L and will also demonstrate that qualitative identifications can be made if the 2,3,7,8-TCDD concentration is 2 ng/L.

Base/neutrals, acids & pesticides

This GC/MS method employs packed columns and requires operating the MS detector in a repetitive scan mode for data acquisition. The reagent water MDL values for 62 of the 72 analytes in Method 625 are given in Table 5. All MDL values are lower than the detection limits specified in the earlier version of this method (*5*). The table includes values for PCB-

TABLE 4

Method detection limit for polycyclic aromatic hydrocarbons as analyzed by Method 610 (*27*)

Compound	Reagent water			Wastewater No. 1 [a]		Wastewater No. 2 [b]	
	Spike level (μg/L)	Average % recovery	MDL (μg/L)	Average % recovery	MDL (μg/L)	Average % recovery	MDL (μg/L)
Napthalene	4.1	104	1.8	83	1.2	80	2.9
Acenaphthylene	8.0	95	2.3	90	2.4	86	4.0
Acenaphthene	4.9	100	1.8	88	1.5	90	1.4
Fluorene	0.80	95	0.21	93	0.22	95	0.25
Phenanthrene	2.0	95	0.64	95	0.61	90	0.79
Anthracene	2.4	96	0.66	96	0.52	92	0.99
Fluoranthene	0.084	130	0.21	107	0.02	114	0.08
Pyrene	0.86	98	0.27	103	0.13	98	0.26
Benzo(*a*)-anthracene	0.081	93	0.01	93	0.01	94	0.02
Chrysene	0.81	95	0.15	95	0.10	96	0.18
Benzo(*b*)-fluoranthene	0.64	97	0.02	98	0.01	98	0.02
Benzo(*k*)-fluoranthene	0.084	95	0.02	93	0.01	95	0.02
Benzo(*a*)-pyrene	0.81	81	0.02	98	0.01	95	0.01
Dibenzo(*a,h*)-anthracene	0.098	88	0.03	102	0.02	112	0.02
Benzo(*g,h,i*)-perylene	0.40	83	0.08	98	0.08	98	0.13
Indeno(1,2,3-*cd*)pyrene	0.15	93	0.04	93	0.03	93	0.04

[a] Refinery effluent.
[b] Coke oven effluent.

1221 and PCB-1254 that were not specified before.

During the MDL study for Method 625, concentration was done using the optional nitrogen blow-down instead of the second micro Kuderna–Danish concentration. Recoveries ranged from 28–94% for the 62 analytes studied; however, only eight analytes gave an average recovery larger than the recovery for that analyte in Methods 604 through 612. There were two instances where the calculated MDL was larger than the spike level. Nineteen values are based on the analysis of eight or 10 aliquots.

Overall, it is best to view the MDL values in Table 5 as initial values subject to refinement through iteration of the MDL procedure. Since the qualitative identification scheme for this mass spectrometer method relies on lower abundance ions with variance not reflected in the calculation of the MDL value, it is possible that qualitative verification might not be made when the analyte is present at a concentration in the neighborhood of MDL. This is another reason to pursue an iteration of the MDL procedure for Method 625.

Comparing the reagent water MDL values for the phenolic analytes common to both Methods 604 and 625 shows that only 4-nitrophenol and pentachlorophenol gave lower MDL values in Method 625.

4-Nitrophenol was spiked at 10 μg/L in the MDL study for Method 625 and at 15.4 μg/L for the Method 604 study. The corresponding spike levels for pentachlorophenol were 10 μg/L and 21 μg/L. Thus, the interaction between instrumental sensitivity and spiking level can be seen to have an effect on the calculated MDL. The remaining phenolic analytes gave MDL values for Method 625 that were between 1.5 and 11 times larger than the corresponding values in Method 604.

The reagent water MDL value for 3,3′-dichlorobenzidine in Method 625 is 250 times larger than that value in Method 605. Since the average recoveries for this analyte are approximately equal in both methods, this large difference reflects instrumental differences in both sensitivity and chromatography. As a rule, amines chromatograph much better under reverse-phase HPLC conditions than gas chromatography conditions. No MDL value for benzidine is reported with Method 625 because of losses experienced in the drying and concentration steps.

In those cases in which the phthalates were spiked at higher concentrations in the Method 625 MDL study compared to the Method 606 study, the MDL values were approximately four to seven times higher than the Method 606 MDL values. Bis(2-ethylhexyl)phthalate was spiked at nearly identical concentrations in both MDL studies and gave nearly identical MDL values. Di-*n*-octyl phthalate was spiked at a lower concentration in the Method 625 MDL study and gave a slightly lower MDL value compared to Method 606.

Method 625 and Method 606 show opposite trends in the average recovery of the phthalates. In Method 625 recovery increases with increasing retention time, but decreases with increasing retention time in Method 606. All Method 625 MDL values are close to the spiking values; therefore, iteration of the MDL procedure for the phthalates may not result in much different MDL values.

The nitroso analyte in the Method 625 MDL study exhibits an MDL value consistent with the differences in instrumental sensitivity between Method 625 and Method 607. In Method 625, the spiking level was 12 times higher than in Method 607 and the calculated MDL value was 17 times higher.

The pesticide analytes that survive the basic extraction step of Method 625 show MDL values between 27 and 1400 times higher than the corresponding values in Method 608. Heptachlor epoxide displayed the least difference and 4,4′-DDE displayed the greatest difference. The average recovery in the Method 625 MDL study is generally lower than that in Method 608; however, no recovery was greater than 100%, as was the case in Method 608. The pesticides α-BHC, γ-BHC, endosulfan I, endosulfan II, and endrin were lost during the basic extraction

step. Large differences in detector sensitivity are responsible for the large differences in MDL between Method 625 and 608.

The MDL values for nitrobenzene and isophorone again show the interplay between the original estimate of MDL and the subsequent value of the calculated MDL. In Method 625, both analytes were spiked into reagent water at concentrations lower than that used in Method 609 and each gave a lower MDL value. Since there is not a great deal of difference between instrumental sensitivity in this case, it is not surprising that the lower estimate for MDL resulted in a lower calculated MDL. In contrast, the dinitrotoluene analytes gave MDL values that were 220 and 320 times larger in Method 625 compared to Method 609. This difference is attributed to the large differences between instrumental sensitivity in these two methods.

Method 625 MDL values for the first three eluting PAH analytes (naphthalene, acenaphthalene, and acenaphthylene) are very similar to the values obtained for Method 610. These three analytes are detected with a UV detector similar in instrumental sensitivity to the mass spectrometer used in Method 625. Naphthalene was the only PAH analyte that gave a lower MDL value in Method 625, but it was also the only analyte spiked at a lower concentration in Method 625 compared to 610. The 13 remaining PAH analytes gave MDL values in Method 625 that were between 3 and 780 times higher than the corresponding values in Method 610. This reflects the differences between the fluorometer and mass spectrometer in detector sensitivity. Benzo(*g*, *h*, *i*)perylene gave an MDL larger than the spike level in the Method 625 study and it was the only PAH in Method 625 that gave an average recovery higher than the corresponding recovery in Method 610.

The haloether analytes in Method 625 gave MDL values consistent with detector sensitivity and spiking level. The calculated MDL for 4-bromophenyl phenyl ether was lower than the value in Method 611, but it was also spiked at a lower level. The remaining haloether analytes gave MDL values ranging from 1.1 to 19 times larger than the corresponding values in Method 611. Clearly, there is no great difference in MDL results between these two methods. The Method 625 haloether recoveries were about half those reported in Method 611.

1,3-Dichlorobenzene gave an anomalous MDL value when compared to the other analytes in Method 625. Highly variable losses were attributed to the volatility of the analyte. The spike level was lower than that in Method 612, but in Method 625 the

TABLE 5

Method detection limits for compounds as analyzed by Method 625 in reagent water (*31*)

Compound	Spike level (µg/L)	Average % recovery	MDL (µg/L)
Acenaphthene	3.8	63	1.9
Acenaphthylene	3.8	47	3.5
Anthracene	3.8	70	1.9
Aldrin	10	72	1.9
Benzo(*a*)anthracene	25	88	7.8
Benzo(*k*)fluoranthene	3.8	80	2.5
Benzo(*a*)pyrene	3.8	73	2.5
Benzo(*g*,*h*,*i*)perylene	3.8	92	4.1
Benzyl butyl phthalate	3.8	74	2.5
Bis(2-chloroethyl) ether	13.3	43	5.7
Bis-(2-chloroethoxy) methane	13.3	45	5.3
Bis(2-ethylhexyl) phthalate	3.8	94	2.5
Bis(2-chloroisopropyl) ether	25	61	6.3
4-Bromophenyl phenyl ether	3.8	66	1.9
2-Chloronaphthalene	3.8	66	1.9
Chrysene	3.8	86	2.5
4-4′-DDD	10	80	2.8
4,4′-DDT	10	63	4.7
Dibenzo(*a*,*h*)anthracene	3.8	82	2.5
Di-*n*-butyl phthalate	3.8	85	2.5
1,3-Dichlorobenzene	3.8	60	4.4
1,4-Dichlorobenzene	13.3	40	5.0
Dieldrin	10	83	2.5
Diethyl phthalate	3.8	64	1.9
Dimethyl phthalate	3.8	49	1.6
2,6-Dinitrotoluene	3.8	64	1.9
Di-*n*-octyl phthalate	3.8	84	2.5
Fluoranthene	3.8	80	2.2
Fluorene	3.8	64	1.9
Heptachlor	10	69	1.9
Heptachlor epoxide	10	82	2.2
Hexachlorobenzene	3.8	67	1.9
Hexachlorobutadiene	3.8	58	0.9
Hexachloroethane	3.8	60	1.6
Indeno(1,2,3-*cd*)pyrene	3.8	85	3.7
Isophorone	3.8	69	2.2
Naphthalene	3.8	70	1.6
Nitrobenzene	3.8	68	1.9
N-Nitroso-di-*n*-propylamine	25	66	8
Pyrene	3.8	79	1.9
1,2,4-Trichlorobenzene	3.8	66	1.9
Benzo(b)fluoranthene[a]	13.3	45	4.8
4-Chlorophenyl phenyl ether[a]	13.3	45	4.2
3,3′-Dichlorobenzidene[a]	33	52	16.5
2,4,-Dinitrotoluene[a]	13.3	44	5.7
PCB 1221[a]	91	77	30
PCB 1254[a]	91	80	36
Phenanthrene[a]	13.3	51	5.4
4-Chloro-3-methylphenol[a]	10	71	3.0
2,4-Dichlorophenol[a]	10	60	2.7
2,4-Dimethylphenol[a]	10	57	2.7
2,4-Dinitrophenol[a]	40	94	42
2-Methyl-4,6-dinitrophenol[a]	40	77	24
4-Nitrophenol[a]	10	52	2.4
Pentachlorophenol[a]	10	87	3.6
Phenol[a]	10	28	1.5
2,4,6-Trichlorophenol[a]	10	64	2.7
βBHC[b]	6	69	4.2
δBHC[b]	6	56	3.1
4,4′-DDE[b]	10	69	5.6
Endosulfan sulfate[b]	7	79	5.6

[a] MDL based on 8 aliquots of reagent water.
[b] MDL based on 10 aliquots of reagent water.

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calculated MDL value was larger than the spike level. Hence the results for this chlorinated hydrocarbon analyte should be regarded with caution.

Conclusions

The purpose of this procedure is to provide a MDL that is used to judge the significance of a single measurement of a future sample. The MDL procedure was formulated to accommodate application to a broad variety of physical and chemical methods. It was necessary to make the procedure device—or instrument—independent to accomplish the wide application desired.

The measurement of the MDL value, in a given matrix, is meaningless if it can be shown by analyte-specific methods that a high background is due to interference rather than the analyte in question. Standard additions in a large neighborhood proximate to the MDL on an interfering background for the purpose of determining the MDL can have value in providing an accuracy and precision statement for the analytical method at analyte levels comparable to the interference concentration in that specific matrix.

The iterative procedure is presented only as a means to overcome mistaken estimates for the MDL. When the analyte is present in the matrix due solely to standard additions and the estimated MDL was found to be outside the 95% confidence interval of the calculated MDL, only one or two iterations should be necessary to identify the MDL with sufficient accuracy. However, only a full regression treatment would provide a more complete description. When economically feasible, the full regression treatment should be used.

If the relative standard deviation of the seven replicates is in the range of 20.5–70.1%, then the estimated MDL will be within the 95% confidence interval of the calculated MDL. This is sufficient statistical evidence to stop the iterative MDL procedure. Should the relative standard deviation fall outside this range, the results are suspect. Experience has shown that when the relative standard deviation is at or near 10%, the calculated MDL values can be below instrumental detection limits.

We can look forward to continued lowering of such performance characteristics as established analytical procedures are adjusted to accommodate future advances in analytical technology. This will serve to push the MDL to lower values than those previously assigned.

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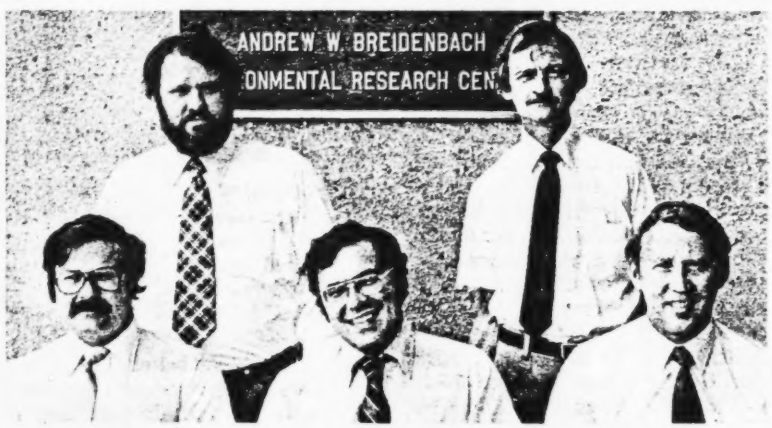
Supplementary Material Available: *Tables 6–14 contain additional Method Detection Limits (MDLs) for the analyses of trace organics in wastewater. Table 6—volatile compounds by Method 601. Table 7—phenols by Method 604 using flame ionization detection. Table 8—pentafluorobenzyl derivatives of phenols by Method 604 using electron capture detection. Table 9—phthalates by Method 606. Table 10—nitrosamines by Method 607. Table 11—nitroaromatics and isophorone by Method 609. Table 12—haloethers by Method 611. Table 13—chlorinated hydrocarbons by Method 612. Table 14—volatile compounds by Method 624 using GC/MS. Photocopies of the supplementary material from this paper or microfiche (105 × 148 mm, 24 × reduction, negatives) may be obtained from Business Operations, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Full bibliographic citation (journal, title of article, author) and prepayment, check or money order for $13 for photocopy ($14.50 foreign) or $4 for microfiche ($5 foreign), are required.*



Standing (left to right) **Stephan A. Quave** *and* **Gerald D. McKee;** *seated (left to right)* **Denis L. Foerst, John A. Glaser,** *and* **William L. Budde.** *The authors are members of the professional staff of the Environmental Monitoring and Support Laboratory (EMSL) at the Andrew W. Breidenbach Environmental Research Center in Cincinnati. Quave is a statistician with the Equivalency Staff, Office of the Director of EMSL. McKee is the section chief of the Inorganic Analyses Section of EMSL. Foerst and Glaser are both research chemists in the Organic Analyses Section of EMSL. Budde is the section chief of the Advanced Instrumentation Section. The authors are engaged in different aspects of analytical method development for trace analytes in water and related matrices.*